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(12) UK Patent Application (19) GB (11) 2 1 1 2 6 2 1 A

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(21) Application No 8219829

(22) Date of filing  
8 Jul 1982

(30) Priority data

(31) 56/209266

(32) 25 Dec 1981

(33) Japan (JP)

(43) Application published  
27 Jul 1983

(51) INT CL<sup>3</sup> C12J 1/00

(52) Domestic classification  
A2B AKC  
U1S 1517 1538 A2B

(56) Documents cited  
GB 0732837  
GB 1547941

(58) Field of search  
A2B

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(54) A powdered vinegar-like composition

(57) A powdery vinegar-like composition can be made by mixing a starch hydrolysate and an acetic acid solution & spray drying the mixture. The starch hydrolysate contains not more than 20 % oligosaccharides having a glucose polymerization degree of not more than 5 and not more than 7% oligosaccharides having a glucose polymerization degree of not more than 3.

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## SPECIFICATION

## Process for powdering a liquid seasoning containing acetic acid

5 The present invention relates to a process for powdering a liquid seasoning containing acetic acid as a principal ingredient which produces powder having a high acetic acid content in high acetic acid yield notwithstanding acetic acid is a volatile ingredient and moreover having a good quality. 5

As a conventional process for powdering a liquid seasoning containing acetic acid, the process of Japanese Patent No. 929540 is already known. This conventional process comprises dissolving a water soluble substance containing as principal ingredient one or more kinds of starch derivatives such as dextrin, gelatinized oxidized starch etc. in a liquid seasoning containing acetic acid in an amount of not less than 70 % of the amount of the water contained in the liquid seasoning containing acetic acid, which the water soluble substance is selected and used under the condition that the solution obtained by dissolving the water soluble substance in an amount of not less than 70 % as described above is able to be spray-dried, and then spray-drying the resulting solution at as low a temperature as possible. According to this conventional process, it was difficult to produce a quality product worthy of calling powder of a liquid seasoning containing acetic acid, because of the defects in various points such as with reference to the process, spray-drying aptitude, acetic acid yield etc., and with reference to the produced powder, caking resistance, acetic acid stability, solubility, viscosity of its solution etc.. Namely, in order to produce the powder, for example, having a high, viz., at least 10 % acetic acid content which does not cause caking, it is good to use a high molecular dextrin or an oxidized starch. However these substances have essentially a high viscosity and the more these substances were dissolved in an aqueous solution of acetic acid in an amount of not less than 70 % of the amount of the water contained in the aqueous solution of acetic acid, the higher the viscosity of each resulting mixture became, and therefore each mixture brought a quite difficult operation on spray-drying. Moreover each aqueous solution of the obtained product had such a high viscosity as was variously an obstacle to its utilization, and the obtained products were not always good in quality in various respects such as acetic acid yield, acetic acid stability, caking resistance etc.. Furthermore, an oxidized starch was very inconvenient to prepare the solution for spray-drying, because of its insolubility in a cold water. 10 15 20 25 30

In order to overcome the foregoing defects, the present inventors before tried to produce a high quality powder of a liquid seasoning containing acetic acid in high yield by using a starch hydrolysate (a starch hydrolysate means hydrolysate of starch) having a limited DE value. It is generally considered that a DE value indicates the properties of the starch hydrolysates prepared variously according to a hydrolyzing extent. However the present inventors could get no satisfactory result by using a starch hydrolysate having a limited DE value, because of the dispersions of acetic acid yield and quality. For example, when various starch hydrolysates having a DE value of about 14, which was considered a preferable DE value from the experience, were prepared and thereby each powder of a liquid seasoning containing acetic acid was produced, not only the dispersion of acetic acid yield but also the dispersions of qualities such as acetic acid stability, caking resistance, solubility etc. in the obtained products were recognized, though the starch hydrolysates having the same DE value of about 14 were used. 35 40 45 50 55 60 65

With a view to eliminating many defects involved in producing powder of a liquid seasoning containing acetic acid, the present inventors went ahead with the research apart from a DE value. Resultingly the present inventors found that among starch hydrolysates containing saccharides having by stages a glucose polymerization degree, the starch hydrolysate containing saccharides having a glucose polymerization degree of 1 to 3 does not possess at all the capacity suitable to a powdering carrier (viz., carrier for powdering) in case of drying the solution comprising a powdering carrier, acetic acid and water as three principal ingredients, and that the starch hydrolysate containing saccharides having a glucose polymerization degree of 4 to 5 possesses an extremely insufficient capacity as a powdering carrier, and that in points of drying property, acetic acid yield and quality, the inferior results are recognized in proportion to the increasing of the content ratio which saccharides having a glucose polymerization degree of not more than 5, especially not more than 3, account for in the starch hydrolysate. Moreover the present inventors found that in the case of the starch hydrolysate containing saccharides having a glucose polymerization degree of about 6 or more, the higher the glucose polymerization degree becomes, the better the capacity as a powdering carrier for acetic acid becomes and the better the storage stabilities of the produced powder such as caking resistance etc. become, and however, when said degree becomes too high, the viscosity increases to result in hindrance on spray-drying, and the increase (the increase is actually done by decreasing an amount of the starch hydrolysate per an amount of water) of an amount of water in order to decrease the viscosity causes the lowering of the yield, and therefore the glucose polymerization degree has its limit. Consequently the present inventors found that the suitable range of glucose polymeriza-

tion degrees in a starch hydrolysate is approximately from 6 to 18 as an average glucose polymerization degree. Namely, the present inventors found that when a starch hydrolysate is mixed in a liquid seasoning containing acetic acid and the resulting solution is spray-dried, an acetic acid yield and quality of produced powder of a liquid seasoning containing acetic acid are influenced by a glucose polymerization degree of the starch hydrolysate, and that when a starch hydrolysate containing not more than 20 % oligosaccharides having a glucose polymerization degree of not more than 5 and not more than 7 % oligosaccharides having a glucose polymerization degree of not more than 3 and having an average glucose polymerization degree of 6 to 18 as a whole is selected and used, there is produced effectively powder of liquid seasoning containing acetic acid having a high acetic acid content of at least 10 % in high acetic acid yield of at least 70 %, and moreover which is of good quality. Furthermore, as the result of the developmental research the present inventors found that it brings a good result that a specifically polymerized oligosaccharide, viz., cyclic oligosaccharide or a starch hydrolysate prepared by hydrolyzing slightly starch composed of amylopectin is used alone or together with other starch hydrolysate under the abovementioned conditions concerning the constitution of glucose polymerization degree.

The present invention was completed on the basis of the abovementioned findings. The present invention is a process for powdering a liquid seasoning containing acetic acid, characterized in that a starch hydrolysate containing not more than 20 % oligosaccharides having a glucose polymerization degree of not more than 5 and not more than 7 % oligosaccharides having a glucose polymerization degree of not more than 3 is mixed in a liquid seasoning containing acetic acid in an amount of not less than 70 % of the amount of the water contained in the liquid seasoning containing acetic acid, and the resulting mixture is spray-dried.

A preferable starch hydrolysate to use in the present invention is such a starch hydrolysate as has an average glucose polymerization degree of 6 to 18 and induces a viscosity of not more than 300 cps at 40°C in the case of its 50% aqueous solution and contains not more than 15% oligosaccharides having a glucose polymerization degree of not more than 5 and not more than 5% oligosaccharides having a glucose polymerization degree of not more than 3. And a starch hydrolysate to use in the present invention is one member or the mixture of two or more members selected from the group consisting of the following a, b, c and d.

- a. a starch hydrolysate prepared by hydrolyzing starch composed of amylopectin and amylose,
- b. a starch hydrolysate prepared by hydrolyzing starch composed of amylopectin,
- c. a starch hydrolysate containing cyclic oligosaccharides and acyclic starch hydrolysate, said a starch hydrolysate being prepared from starch composed of amylopectin and amylose, and
- d. a starch hydrolysate containing cyclic oligosaccharides and acyclic starch hydrolysate, said a starch hydrolysate being prepared from starch composed of amylopectin.

A starch hydrolysate containing at least one member selected from the group consisting of a  $\alpha$ -cyclic oligosaccharide,  $\beta$ -cyclic oligosaccharide and  $\gamma$ -cyclic oligosaccharide, said at least one member being added, is able to be used in the present invention. Said  $\alpha$ -cyclic oligosaccharide,  $\beta$ -cyclic oligosaccharide or  $\gamma$ -cyclic oligosaccharide is obtained by separating and purifying from a starch hydrolysate containing cyclic oligosaccharides formed by making a cyclic oligosaccharide-forming enzyme act on a gelatinized or liquefied starch.

The average polymerization degree in the present invention is based on the value obtained by dividing the whole amount of a starch hydrolysate by the amount of the reducing sugar contained in the starch hydrolysate in the case of the starch hydrolysate not containing cyclic oligosaccharide, and in the case of a starch hydrolysate containing cyclic oligosaccharide is based on the total value obtained by adding the value obtained by multiplying the average polymerization degree of the cyclic oligosaccharides by the content ratio which the cyclic oligosaccharides account for in the starch hydrolysate to the value obtained by multiplying the average polymerization degree of acyclic saccharides, said average polymerization degree being obtained by the abovementioned way, by the content ratio which the acyclic saccharides account for in the starch hydrolysate. And G stands for glucose and the suffix number stands for a polymerization degree. For example,  $G_1$ ,  $G_2$  and  $G_3$  stand for in due order glucose, maltose and maltotriose, and  $G_4$  stands for oligosaccharide having a polymerization degree of 4, and  $G_n$  to n stands for saccharides having a polymerization degree of not less than 9.

The starch hydrolysate prepared by hydrolyzing an ordinary starch composed of amylopectin and amylose to use in the present invention, which contains not more than 20 % oligosaccharides having a glucose polymerization degree of not more than 5 and not more than 7 % oligosaccharides having a glucose polymerization degree of not more than 3 and at the same time has an average polymerization degree of 6 to 18, is prepared by the undermentioned methods and is used alone or together with two or more kinds of starch hydrolysates prepared by said undermentioned methods. Further starch hydrolysates prepared by other methods can be used so long as the intended powder of the present invention can be produced.

(A) A method comprising subjecting a starch hydrolysate (it is preferable that a starch hydrolysate having a DE value of 6 to 20, which is prepared by hydrolysis with acid or enzyme,

is mainly used.) prepared by a usual hydrolysis with acid or enzyme to fractionating with an aqueous alcohol solution and separating and removing unnecessary components to obtain the abovementioned constitution of glucose polymerization degree.

- (B) A method for preparing a starch hydrolysate by subjecting starch to the specific two-staged liquefaction (when a starch hydrolysate prepared by the first staged hydrolysis has a DE value of not more than 3, the starch hydrolysate is subjected to heating and boiling, and in the second staged hydrolysis the starch hydrolysate is further hydrolyzed with  $\alpha$ -amylase added to have a DE value of 6 to 16.) 5

- (C) A method comprises making a microorganism such as yeast etc. assimilate glucose, maltose and maltotriose contained in a starch hydrolysate (it is preferable that a starch hydrolysate having a DE value of approximately 10 to 20, which is prepared by hydrolysis with enzyme, is mainly used.) prepared by a conventional method. 10

- When in the present invention the starch hydrolysate having an average glucose polymerization degree of 6 to 18 and containing not more than 20 % oligosaccharides having a glucose polymerization degree of not more than 5 and not more than 7 % oligosaccharides having a glucose polymerization degree of not more than 3 is used as a powdering carrier, the undermentioned (II) a starch hydrolysate prepared by hydrolyzing starch composed of amylopectin or (III) a starch hydrolysate prepared by hydrolyzing an ordinary starch is used alone, and moreover the abovementioned use is characterized in that the effects in the production of intended powder can be more heighten by the specific combined use constituted by selecting members from the group comprising (I) cyclic oligosaccharides having polymerization degree of 6 to 8 which are prepared by hydrolyzing specifically starch, (II) a starch hydrolysate having an average polymerization degree of 6 to 50 which is prepared by hydrolyzing starch composed of amylopectin, (III) a starch hydrolysate having an average polymerization degree of 6 to 18 which is prepared by hydrolyzing an ordinary starch, and so on, viz., said combined use is (I) + (II), (I) + (III), (II) + (III), (I) + (II) + (III) etc.. 15 20 25

The abovementioned specified starch hydrolysates are explained in points of each and their combined usings as follows:

(I) Cyclic oligosaccharides:

- 30 The starch hydrolysate (viz., mixture of cyclic oligosaccharides (I) and acyclic starch hydrolysate (II)) containing acyclic starch hydrolysate and cyclic oligosaccharide (polymerization degree: 6 to 8) made up by cyclically transforming of oligosaccharides having a glucose polymerization degree of 6, 7 or 8, said cyclic oligosaccharides being formed by making a cyclic oligosaccharide-forming enzyme act on a gelatinized or liquefied starch, can be easily dissolved in an aqueous solution of acetic acid, and the resulting solution has a low viscosity. Therefore by spray-drying the solution obtained by mixing the starch hydrolysate in a aqueous solution of acetic acid, the present inventors found that the spray-drying can be smoothly done because of a low viscosity, and that one of basic techniques of the present invention, which is dissolving a powdering carrier in an aqueous solution of acetic acid in an amount of not less than 70 %, as much as possible, of the amount of the water contained in the aqueous solution of acetic acid, can be more heighten, and that the acetic acid yield of the obtained powder can be heighten and the obtained powder containing acetic acid is very excellent in point of storage stability. 35 40

- Cyclic oligosaccharide, which has a glucose polymerization degree of 6, 7 or 8 is obtained by separating and purifying from a starch hydrolysate containing cyclic oligosaccharide formed by making a cyclic oligosaccharide-forming enzyme act on a gelatinized or liquefied starch, can not be used alone as a powdering carrier of the low stability in an aqueous solution of acetic acid. However, so long as said purified cyclic oligosaccharide is used in such an amount that said purified cyclic oligosaccharide can be dissolved and moreover the resulting mixture has an average polymerization degree of 6 to 18, the object of the present invention can be fulfilled by using said purified cyclic oligosaccharide together with one member or more selected from the group consisting of an ordinary starch hydrolysate (III) prepared by hydrolysis according to the object of the present invention, a starch hydrolysate (II) prepared by specifically hydrolyzing starch composed of amylopectin, and mixture (I + II) containing cyclic oligosaccharides and acyclic starch hydrolysate, said mixture being prepared by making a cyclic oligosaccharide-forming enzyme act on starch. As a powdering carrier in the present invention, cyclic oligosaccharide is used in such an amount that said cyclic oligosaccharide can be dissolved, and the preferable amount is approximately 5 % or more of a whole powdering carrier. In the case of using of plural kinds of cyclic oligosaccharide the preferable amount is the total amount of them. 45 50 55

- 60 (II) A starch hydrolysate prepared by hydrolyzing starch compound of amylopectin: 60  
When starch composed of amylopectin such as glutinous corn starch, glutinous rice starch etc. is hydrolyzed with  $\alpha$ -amylase, an amylopectin polymer begins to be cut at  $\alpha$ -1, 4 glucoside linkage. In that case the hydrolysis begins with the intermediate position of the straight chain of amylopectin at the early stage, and thus the initial polymer changes gradually into still less small polymers, retaining the branched polymeric structure. The starch hydrolysate prepared by 65

hydrolyzing amylopectin with  $\alpha$ -amylase begins drastically lowering of its velocity when it has an average polymerization degree of approximately 50 to 70, and when said starch hydrolysate has an average polymerization degree of 6 to 50, it has a lower viscosity than that of a starch hydrolysate prepared by hydrolyzing an ordinary starch composed of amylose and amylopectin, and said starch hydrolysate having an average polymerization degree of 6 to 50 can be easily dissolved in an aqueous solution of acetic acid and does not have a retrogradation property.

When the starch hydrolysate (II) having an average polymerization degree of 6 to 50, which is prepared by hydrolyzing starch composed of amylopectin, is used alone as a powdering carrier in the present invention, the starch hydrolysate having an average polymerization degree of 6 to 18 and containing not more than 20 % oligosaccharides having a glucose polymerization degree of not more than 5 and not more than 7 % oligosaccharides having a glucose polymerization degree of not more than 3 is selected and used, and when the starch hydrolysate has said conditions concerning polymerization, the branched structures of amylopectin can be maintained and the spray-drying aptitude is good because of the lower viscosity than that of starch hydrolysate prepared by hydrolyzing starch containing amylose in the same extent as in the case of said starch composed of amylopectin, and moreover because said starch hydrolysate can be mixed in an aqueous solution of acetic acid in a rich amount, the acetic acid yield of the obtained powder is good, and the storage stability of the obtained powder is good. Further, when said starch hydrolysate derived from amylopectin is used together with other starch hydrolysate, said starch hydrolysate derived from amylopectin, having an average polymerization degree of 10 to 50 is mainly used selectively among said starch hydrolysates having an average polymerization degree of 6 to 50, and when said starch hydrolysate derived from amylopectin is used together with at least one member selected from the group consisting of a starch hydrolysate (III) prepared by hydrolyzing an ordinary starch, cyclic oligosaccharides (I) and the mixture of cyclic oligosaccharides (I) and acyclic starch hydrolysate (II), the intended object of the present invention can be fulfilled so long as the resulting mixture has as a powdering carrier an average polymerization degree of 6 to 18 and contains not more than 20 % oligosaccharides having a glucose polymerization degree of not more than 5 and not more than 7 % oligosaccharides having a glucose polymerization degree of not more than 3.

Furthermore, in the present invention a high-molecular water-soluble substance such as gum arabic, gelatin, CMC etc. can be added.

In the present invention the above-explained starch hydrolysate is mixed in a liquid seasoning containing acetic acid in an amount of 70 to 200 % of the amount of the water contained in said liquid seasoning and thereafter subjected to spray-drying.

A liquid seasoning containing acetic acid to use in the present invention is selected from acid liquid seasonings, in which acetic acid is a principal ingredient, such as rice vinegar, "kasuzu" made by subjecting "sake cake" as a main raw material to an acetic acid fermentation, "shuseizu" prepared by subjecting an aqueous ethyl alcohol solution to an acetic acid fermentation, malt vinegar, wine vinegar, cider vinegar, synthesized vinegar, sauce, aqueous solution of acetic acid, concentrated solution of each abovementioned matter, each abovementioned matter added with acetic acid in addition, processed solution of each abovementioned matter etc..

Further, when a liquid seasoning containing acetic acid is powdered, various aroma ingredients other than acetic acid also powdered at the same time. The yield (aroma remaining ratio) of low boiling aroma ingredients which are contained in the abovementioned brew vinegars etc. is approximately in proportional to an acetic acid yield, and therefore the increase of an acetic acid yield is very important for keeping aroma ingredients.

Hereinafter the tests and examples of the present invention are described.

#### Test 1:

By using starch hydrolysate (dried matter) A, B, C, D, E, F, G, H and I having respectively analytical values shown in Table 1, the solutions (40°C) comprising 100 parts of starch hydrolysate, 25 parts of acetic acid and the given parts of water are severally prepared and then each resulting solution was spray-dried at a chamber temperature of 87°C, being heated up to 60°C by a plate heater just before spray-drying. The thus powders containing acetic acid were produced, of which results are shown in Table 2. And starch hydrolysates used as a sample were respectively prepared by the following methods.

Sample A: the starch hydrolysate having a DE value of 17.9 prepared by hydrolyzing with acid and enzyme, said starch hydrolysate being an article on the market,

Sample B: the starch hydrolysate having a DE value of 14.5 prepared by hydrolyzing with enzyme and enzyme, said starch hydrolysate being an article on the market,

Sample C: the starch hydrolysate having a DE value of 14.1 prepared by the following process: emulsion of a corn starch was added with  $\alpha$ -amylase and hydrolyzed till the DE value reached 1.5, and when the DE value reached 1.5 the hydrolysate was heated up to 130°C and more maintained at 130°C for 10 minutes, and thereafter the hydrolysate was cooled and added

again with  $\alpha$ -amylase to proceed with the hydrolysis till the DE value reached 16.8. And by making yeast assimilate glucose, maltose and maltotriose contained in the hydrolysate having a DE value of 16.8, the starch hydrolysate having a DE value 14.1 was prepared,

5 Sample D: the starch hydrolysate having a DE value of 13.9 prepared by hydrolyzing with acid, said starch hydrolysate being an article on the market, 5

Sample E: the starch hydrolysate having a DE value of 11 prepared from emulsion of a corn starch with  $\alpha$ -amylase by the same two-staged liquefaction as in the case of Sample C, viz., hydrolyzing was proceeded till a DE value of 1.5 in the first stage and till a DE value of 11 in the second stage,

10 Sample F: the starch hydrolysate having a DE value of 8.2 prepared in the same manner as in the case of Sample E excepting that hydrolyzing was proceeded till a DE value of 8.2 in the second stage, 10

Sample G: the starch hydrolysate having a DE value of 6.4 prepared in the same manner as in the case of Sample E excepting that hydrolyzing was proceeded till a DE value of 6.4 in the second stage, 15

Sample H: the starch hydrolysate having a DE value of 5.6 prepared in the same manner as in the case of Sample E excepting that hydrolyzing was proceeded till a DE value 5.6 in the second stage,

20 Sample I: the starch hydrolysate having a DE value of 4.5 prepared in the same manner as in the case of Sample E excepting that hydrolyzing was proceeded till a DE value of 4.5 in the second stage. 20

By using glucose which was an article on the market, maltose (saccharide composition: 95 % maltose and 5 % glucose) which was an article on the market, maltotriose (saccharide composition: 90 % maltotriose and 5 % maltohexaose) prepared by hydrolyzing pullulan (pullulan PF-10 supplied by Hayashibara Co., Ltd.) with pullulanase (CK 20-L supplied by Amano Pharmaceutical Co., Ltd.) and the starch hydrolysate (0.4 % G<sub>1</sub>, 1.3 % G<sub>2</sub>, 15.4 % G<sub>3</sub>, 25.2 % G<sub>4</sub>, 20.6 % G<sub>5</sub>, 15.8 % G<sub>6</sub>, 9.5 % G<sub>7</sub>, 4.2 % G<sub>8</sub> and 7.6 % G<sub>9 to n</sub>) containing mainly maltotetraose and maltopentaose, said starch hydrolysate being prepared as follows: the abovementioned Sample A was subjected to assimilating by yeast and thereby glucose, maltose and maltotriose were assimilated to a certain extent by yeast and the thus treated Sample A was fractionated using an aqueous solution of ethyl alcohol, each mixed solution as shown in Table 3 was prepared and spray-dried at a chamber temperature of 87°C. The obtained results are shown in Table 3. 25

The saccharide composition, the viscosity and the acetic acid yielded in the present invention were determined by the following ways. 35

Saccharide composition: the saccharide composition was determined qualitatively and quantitatively by the liquid chromatography using PNH<sub>2</sub>-10/S2504 (supplied by Shimadzu Corporation) as a column, an acetonitrile-water as a mobile phase and a differential refractometer as a detector.

40 Viscosity: the viscosity of the aqueous solution of the starch hydrolysate was determined as follows: 500 g of a sample (starch hydrolysate) was dissolved in 500 g water and the resulting solution was subjected to measuring its viscosity at 40°C by a cylinder-type rotational viscometer And the viscosity of solution before spray-drying also was determined in the same way. 40

45 Acetic acid yield: the acetic acid yield was calculated according to the following formula: Acetic acid yield (remaining ratio) % = 45

$$50 \quad \frac{B}{C} \times D \times \frac{100}{A} \quad 50$$

wherein A stands for the amount of acetic acid used, B stands for the amount (solid matter) of the starch hydrolysate used, C stands for the solid content (%) of the produced powder containing acetic acid and D stands for the acetic acid content (%) of the produced powder containing acetic acid. 55

Table 1

Sample	Saccharide composition (%)									Average Poly- merization Degree	Viscosity (cps)
	G <sub>1</sub>	G <sub>2</sub>	G <sub>3</sub>	G <sub>4</sub>	G <sub>5</sub>	G <sub>6</sub>	G <sub>7</sub>	G <sub>8</sub>	G <sub>9</sub> to n		
A	4.8	5.7	5.6	5.6	5.4	5.1	4.7	4.1	59.0	5.6	40
B	0.8	5.2	7.0	5.4	4.8	9.8	8.7	5.3	53.0	6.9	42
C	trace	trace	7.3	6.8	6.6	14.7	12.9	5.7	46.0	7.1	43
D	3.7	4.4	4.3	4.2	3.9	3.2	3.0	3.3	70.0	7.2	71
E	trace	2.3	4.6	4.4	4.4	6.5	7.5	6.9	63.4	9.1	63
F	trace	1.2	2.7	2.7	2.3	4.4	5.7	5.3	75.7	12.2	145
G	trace	1.2	2.6	2.3	1.8	3.5	4.1	2.7	81.8	15.6	180
H	trace	0.5	1.3	1.8	1.8	2.9	3.8	2.6	85.3	17.9	200
I	trace	0.4	0.6	0.8	0.6	2.0	2.7	2.6	90.3	22.2	420

Table 2

(100 parts of the starch hydrolysate and 25 parts of acetic acid were used.)

Amount of water (parts)	Sample									
	Test item									
	A	B	C	D	E	F	G	H	I	
100	37	39	42	59	55	82	104	140	290	Viscosity of solution (cps)
	14.3	15.0	16.3	15.8	17.3	17.5	17.2	Note.1.	Note 1.	Acetic acid content of the produced powder (%)
	69.2	73.2	80.8	77.8	86.8	88.0	86.2			Acetic acid yield
	--	-	±	-	+	+	+			Caking resistance of the produced powder



Table 2 (continued)

Amount of water (parts)	Test item	Sample								
		A	B	C	D	E	F	G	H	I
130	Viscosity of solution (cps)	19	20	22	29	27	40	51	60	140
	Acetic acid contents of the produced powder (%)	12.3	12.7	14.2	13.8	15.6	16.3	16.4	16.3	Note 1.
	Acetic acid yield (%)	58.1	60.3	68.6	66.3	76.7	80.8	81.4	80.8	
	Caking resistance of the produced powder	--	-	±	-	+	+	+	+	

Table 2 (cont'd)

Amount of water ( parts )	Test Item	SAMPLE									
		A	B	C	D	E	F	G	H	I	
160	Viscosity of solution (cps)	11	12	13	18	17	23	29	32	75	
	Acetic acid content of the produced powder	9.3	9.7	10.3	10.9	12.0	12.5	12.9	13.4	13.8	
	(%)										
	Acetic acid yield (%)	42.4	44.4	47.5	50.6	56.5	59.2	61.4	64.1	66.3	
	Caking resistance of the produced powder	--	-	+	-	+	+	+	+	+	

Note 1 : Spray-drying was impossible because of high viscosity.

Caking resistance : the caking resistance was determined by the result obtained by the method comprising enclosing the produced powder in an aluminium foil pouch and the treated pouch was allowed to stand for 48 hours at 40°C for the storage test.

+ stands for no caking, + stands for a slight caking,  
- stands for caking and -- stands for a hard caking.

Table 2 gives the following explanations.

(1) In the case of Sample A, which had a small average polymerization degree, viz., 5.6 and had 16.1 % the total content of  $G_1$  and  $G_3$  and 27.1 % the total content of  $G_1$  to  $G_5$ , the spray-drying aptitude and the powder yield were very poor and moreover the produced powder was very poor at the caking resistance.

(2) Though Sample B, C and D had a DE value of about 14, the comparisons in points of the acetic acid yield and the caking resistance were as follows: the use of Sample B which had 13.0 % the total content of  $G_1$  to  $G_3$  and 23.2 % the total content of  $G_1$  to  $G_5$  gave the worst results among three produced powders in both the acetic acid yield and the caking resistance, and Sample D which had 12.4 % the total content of  $G_1$  to  $G_5$  and 20.5 % the total content of  $G_1$  to  $G_5$  secured the acetic acid yield in the case of 100 parts water to 100 parts of the starch hydrolysate, however therein the caking resistance was poor, and Sample C which had 7.3 % the total content of  $G_1$  to  $G_3$  and 20.7 % the total content of  $G_1$  to  $G_5$  gave the better yield of acetic acid and the better caking resistance in comparison with those of Sample D, however therein the caking resistance was still slightly poor.

(3) Sample E, F and G which had in turn an average polymerization degree of 9.1, 12.2 and 15.6 and had not more than 20 % the total content of  $G_1$  to  $G_5$  gave good results in all the points such as spray-drying aptitude, acetic acid yield, caking resistance etc. in the case of not more than 130 parts of water to 100 parts of the starch hydrolysate (viz., 77 parts of the starch hydrolysate to 100 parts of water). However it is found that when the amount of the starch hydrolysate to the amount of water is decreased, the acetic acid yield is considerable lowered.

(4) Sample H having an average polymerization degree of 17.9 had a high viscosity. Therefore the solution obtained by mixing 100 parts of the starch hydrolysate and 100 parts of water could not be mechanically spray-dried because of the high viscosity of the solution. In the case of the solution obtained by mixing 100 parts of the starch hydrolysate and 160 parts of water, said solution being able to be spray-dried, the acetic acid yield was poor, and in the case of the solution obtained by mixing 100 parts of the starch hydrolysate and 130 parts of water, said solution being able to be spray-dried, the acetic acid yield was 80.8 %. Sample I having an average polymerization degree of 22.2 induced a difficult spray-drying and a poor yield of acetic acid.

As shown in Table 3, in the case of maltotriose ( $G_3$ ), not to mention glucose and maltose, the solution had a very poor spray-drying aptitude, viz., the spray-dried matters were adhered to a chamber wall and therefore the powder could not be obtained. This state can be guessed by the fact that maltotriose is dissolved in a 97 % aqueous solution of acetic acid. In the case of the starch hydrolysate containing a small quantity of the saccharides of  $G_1$  to  $G_3$  and about 50 % the saccharides of  $G_4$  to  $G_5$ , the solution had a very poor spray-drying aptitude and the obtained powder was very poor at the acetic acid yield and the caking resistance, and it is understood that the saccharides having a glucose polymerization degree of 4 to 5 is hardly suitable as a powdering carrier for covering and keeping acetic acid.

Table 3

In the case of glucose, maltose, maltotriose and the starch hydrolysate mainly containing G<sub>4</sub> to G<sub>5</sub>

(Composition of the solution: acetic acid : water : saccharide = 25 : 100 : 100)

Carrier	Acetic acid		Drying state
	content (%)	Acetic acid yield (%)	
Glucose ( G <sub>1</sub> )	-	-	All adhered to a chamber wall and therefore the powder could not be obtained.
Maltose ( G <sub>2</sub> )	-	-	Ditto
Maltotriose ( G <sub>3</sub> )	-	-	Ditto
Starch hydrolysate mainly containing G <sub>4</sub> to G <sub>5</sub>	8	36	The adherence to a chamber wall was observed and the obtained powder was poor at caking resistance.

Consequently, by judging synthetically the present inventors found that the starch hydrolysate, which contains not more than 20 % oligosaccharides having a glucose polymerization degree of not more than 5 and not more than 7 % the total content of glucose, maltose and maltotriose, and has an average glucose polymerization degree of 6 to 18 as a whole, is  
 5 selected and mixed in an aqueous solution of acetic acid in an amount of approximately 70 %  
 or more of the amount of the water contained in the aqueous solution of acetic acid and the  
 resulting solution is spray-dried at as low a temperature as possible and thereby the powder  
 containing acetic acid, which has a high acetic acid content and a high acetic acid yield, can be  
 produced and moreover the thus obtained powder is very good at caking resistance, moisture  
 10 proof, keeping or aroma, solubility in water etc.. 10

#### Test 2:

The starch hydrolysates used and their saccharide compositions are as follows:

- \*  $\alpha$ -cyclodextrin obtained by separating and purifying from the liquefied solution containing  
 15 the cyclic oligosaccharides prepared by making a cyclic oligosaccharide-forming enzyme act on a 15  
 potato starch:  
   the cyclic oligosaccharide (100 %  $\alpha$ ) - - - - (I)-A,  
   \* The mixture containing 50 % the starch hydrolysate (acyclic) having an average polymeriza-  
   tion degree of 11.8 and 50 % the cyclic oligosaccharide (mixture of 60 %  $\alpha$ , 25 %  $\beta$  and 15 %  
 20  $\gamma$ ) obtained by making  $\alpha$ -amylase act on a potato starch and thereafter by making a cyclic 20  
 oligosaccharide-forming enzyme act on:  
   the cyclic oligosaccharides (60 %  $\alpha$ , 25 %  $\beta$  and 15 %  $\gamma$  - - - - (I)-B,  
   the starch hydrolysate having an average polymerization degree of 11.8 - - - - (III)-E,  
   \* the two kinds of starch hydrolysates having respectively an average polymerization degree of  
 25 12.5 and 25.0 which were prepared by hydrolyzing a waxy starch (composed of amylopectin): 25  
   the starch hydrolysate having an average polymerization degree of 12.5 which was prepared  
   by hydrolyzing starch composed of amylopectin - - - - (II)-A,  
   the starch hydrolysate having an average polymerization degree of 25.0 which was prepared  
   by hydrolyzing starch composed of amylopectin - - - - (II)-B,  
 30 \* the four kinds of starch hydrolysates having respectively an average polymerization degree of 30  
   5.0, 7.6, 11.8 and 13.3 which were prepared by hydrolyzing a potato starch (composed of  
   amylose and amylopectin) with  $\alpha$ -amylase:  
   the starch hydrolysate having an average polymerization degree of 5.0 - - - - (III)-A,  
   the starch hydrolysate having an average polymerization degree of 7.6 - - - - (III)-B,  
 35 the starch hydrolysate having an average polymerization degree of 11.8 - - - - (III)-C, 35  
   the starch hydrolysate having an average polymerization degree of 13.3 - - - - (III)-D.

Table 4

## Saccharide composition (%)

Powdering carrier	<u>G<sub>1</sub></u>	<u>G<sub>2</sub></u>	<u>G<sub>3</sub></u>	<u>G<sub>4</sub></u>	<u>G<sub>5</sub></u>	<u>G<sub>6</sub></u>	<u>G<sub>7</sub></u>	<u>G<sub>8</sub></u>	<u>G<sub>9 to n</sub></u>
(III)-E	0.6	3.5	5.0	4.5	4.0	6.5	6.0	4.0	65.9
(II)-A	trace	1.4	2.2	1.6	2.4	5.0	5.9	4.6	76.9
(II)-B	trace	0.3	0.6	0.6	0.5	1.2	1.6	1.8	93.4
(III)-A	4.7	6.5	6.9	6.7	6.5	6.0	5.4	4.8	52.5
(III)-B	1.3	2.3	4.5	4.4	4.1	5.5	5.2	4.6	68.1
(III)-C	0.5	1.2	2.7	2.7	2.3	4.4	5.7	5.3	75.2
(III)-D	0.5	1.0	2.6	2.5	2.1	4.0	5.0	4.6	77.7

At least one member selected from the group of abovementioned starch hydrolysates was mixed in an aqueous 20 % acetic acid solution in an amount of 125 % of the amount of the water contained in the aqueous 20 % acetic acid solution and the resulting solution was spray-dried at a chamber temperature of 95°C. In this test, spray-drying state, acetic acid yield, acetic acid stability and caking resistance of the produced powder were observed and the results were shown as in Table 5. 5

Table 5 teaches as follows:

- 1) Tests No. 1 to No. 4 which respectively used the starch hydrolysate prepared by hydrolyzing an ordinary starch composed of amylose and amylopectin, are explained as follows. 10
- In the case of Test No. 1 which used the starch hydrolysate (III)-A having a low average polymerization degree and containing not less than 20 % the saccharides of G<sub>5</sub> or less, the spray-drying aptitude has not a defect at all because of a low viscosity. However a poor performance in converging acetic acid, adherence to chamber wall during spray-drying and a poor remaining ratio of acetic acid are recognized. In addition the produced powder is very poor at 15
- both acetic acid stability and caking resistance. 15
- In the case of Test No. 4 which used the starch hydrolysate (III)-D having a high average polymerization degree, the spray-drying is impossible because of a high viscosity when the amount of the powdering carrier is 125 % of the amount of the water, and therefore the powder can not be produced. In the case of Test No. 3 which used the starch hydrolysate (III)-C having 20
- a lower viscosity than that of the starch hydrolysate (III)-D, a considerably good acetic acid yield, 20
- a good caking resistance and a good acetic acid stability are recognized in the produced powder, though the spray-drying aptitude is slightly bad because the viscosity is still slightly high. However, it is very difficult to secure a higher acetic acid yield than that of Test No. 3, because the starch hydrolysate (III)-C can not be mixed in an aqueous solution of acetic acid in a higher 25
- amount to an amount of the water contained in an aqueous solution of acetic acid than that of 25
- Test No. 3. In the case of Test No. 2 which used the starch hydrolysate (III)-B having an average polymerization degree situated between that of the starch hydrolysate (III)-A and that of the starch hydrolysate (III)-C, the spray-drying aptitude and the acetic acid yield are considerably good, but an inferior caking resistance and an inferior acetic acid stability are recognized. 30
- 2) In the cases of Tests No. 5 and No. 6 wherein Test No. 5 used the mixture of the cyclic oligosaccharides (I)-B and the starch hydrolysate (III)-E having an average polymerization degree of 11.8 and Test No. 6 used the mixture of the former two (viz., (I)-B and (III)-E and the starch hydrolysate (III)-C having a polymerization degree of 11.8, a good spray-drying aptitude, a remarkably heightened acetic acid yield and acetic acid stability, and a good caking resistance 35
- are recognized in each Test, because the cyclic oligosaccharides are not viscous and moreover possess a certain combining property to acetic acid. After further examination, a higher acetic acid yield was obtained by increasing more the amount of the powdering carrier to the amount of the water contained in the aqueous solution of acetic acid on condition that the powdering carrier has the same mixing proportion of ingredients in each powdering carrier of Tests No. 5 40
- and No. 6, and the spray-drying can be performed. 40
- 3) In the case of Test No. 7 wherein the cyclic oligosaccharide ( $\alpha$ -cyclodextrin) (I)-A was used alone on trial as a powdering carrier, the cyclic oligosaccharide was not dissolved to result in settling.
- 4) Tests No. 8 to No. 10 used the starch hydrolysate having an average polymerization 45
- degree of 12.5 (II)-A which was prepared by hydrolyzing a waxy starch. This starch hydrolysate 45
- has approximately the same viscosity as that of the starch hydrolysate having an average polymerization degree of 9 prepared by hydrolyzing an ordinary starch composed of amylose and amylopectin and has a low viscosity in spite of a high average polymerization degree and moreover retains the branched polymeric structures peculiar to amylopectin.
- All the three uses, viz., the combination use (Test No. 8) of the starch hydrolysate (II)-A 50
- having an average polymerization degree of 12.5 derived from amylopectin and the cyclic oligosaccharide (I)-A, the single use (Test No. 9) of the starch hydrolysate (II)-A derived from amylopectin and the combination use (Test No. 10) of the starch hydrolysate (II)-A derived from amylopectin and the starch hydrolysate (III)-C having an average polymerization degree of 11.8 55
- which (III)-C is the same starch hydrolysate as in Test No. 3, produced the superior results in all 55
- points such as spray-drying aptitude, acetic acid yield, acetic acid stability and caking resistance to the results of Tests No. 1 to No. 4. Especially Test No. 8 produced the good results.
- Test No. 11 used the starch hydrolysate (II)-B having an average polymerization degree of 25.0 which was obtained by hydrolyzing a waxy starch. Said starch hydrolysate has a 60
- considerably high viscosity and therefore can not be used much. However the combination use 60
- of said starch hydrolysate and the starch hydrolysate (III)-B having defects in using alone, produced the good results making up the defects of the starch hydrolysate (III)-B.
- In the case of Test No. 12 wherein the abovementioned (II)-B was used much, the spray-drying could not be done because of the very high viscosity.
- 5) Test No. 13 wherein the properties of the cyclic dextrin (I)-B, the starch hydrolysate (III)-E 65

having the average polymerization degree of 11.8 and the starch hydrolysate (II)-A derived from amylopectin were effectively incorporated in the composition of the powdering carrier, produced the best results in all the Tests in all points such as spray-drying aptitude, acetic acid yield, acetic acid stability and caking resistance.

- 5 \* Acetic acid yield is calculated as follows: multiplying an acetic acid content ratio of a produced powder by an amount by weight of a produced powder gives a value, viz., an amount by weight of a remaining acetic acid and then which divided by an amount by weight of acetic acid contained in an aqueous acetic acid solution used and moreover multiplied by 100 is the acetic acid yield. 5
- 10 \*\* Acetic acid stability is calculated as follows: 50 g of a produced powder is enclosed in a pouch (thickness: 0.05 mm) made of polyethylene, said pouch being easily pervious to a gaseous acetic acid, and the pouch is hermetically sealed and then is stored at 35°C for 8 days in a constant temperature box and thereafter an amount of acetic acid contained in a stored powder is measured and the acetic acid stability is calculated by the following equation: 10
- 15 Amount of acetic acid contained in powder after storage 15
- $\frac{\text{Amount of acetic acid contained in powder after storage}}{\text{Amount of acetic acid contained in powder before storage}} \times 10 = \text{Acetic acid stability}$
- 20 Amount of acetic acid contained in powder before storage 20

\*\*\* Caking resistance is judged as follows: a produced powder is enclosed in a pouch made of aluminum foil and the pouch is hermetically sealed and then is stored at 40°C for 10 days and thereafter a caking state is observed.



Test No.

1	2	3	4
-	-	-	-
-	-	-	-
-	-	-	-
-	-	-	-
100 Kg	-	-	-
-	100 Kg	-	-
-	-	100 Kg	-
-	-	-	100 Kg
-	-	-	-
5.0	7.6	11.8	13.3
20 Kg	20 Kg	20 Kg	20 Kg
80 Kg	80 Kg	80 Kg	80 Kg
good	good	good	good
45	57	147	190
Note 2	good	Note 3	Note 4
101.2	115.4	113.3	-
12.5	15.1	14.8	-
63.3	87.1	83.8	-
60	70	75	-
Note 5	caking	Note 6	-

Note 4 : impossible

Note 5 : hard caking

Note 6 : no caking

Table 5

Powdering carrier  
 (I)-A cyclic dextrin (100%)  
 (I)-B cyclic dextrin (60%, 25%, 15%)  
 (II)-A dextrin having an average polymerization degree of 12.5 derived from amylopectin  
 (II)-B dextrin having an average polymerization degree of 25.0 derived from amylopectin  
 (III)-A dextrin having an average polymerization degree of 5.0  
 (III)-B dextrin having an average polymerization degree of 7.6  
 (III)-C dextrin having an average polymerization degree of 11.8  
 (III)-D dextrin having an average polymerization degree of 13.3  
 (III)-E dextrin having an average polymerization degree of 11.8

Average polymerization degree of a powdering carrier

Amount of acetic acid

Amount of water

Solubility of a powdering carrier

Viscosity of solution cps (40°C)

Spray-drying aptitude

Amount of a produced powder (Kg)

Acetic acid content of a produced powder (%)

Acetic acid remaining ration (yield) \* (%)

Acetic acid stability (ratio) \*\* (%)

Caking resistance \*\*\*

Note 1 : insoluble and settling

Note 2 : adherence to a chamber wall

Note 3 : slightly bad because of a high viscosity

Table 5 (continued)

Powdering carrier	Test No.			
	5	6	7	8
(I)-A cyclic dextrin (100%)	-	-	100 Kg	10 Kg
(I)-B cyclic dextrin (60% $\alpha$ , 25% $\beta$ , 15% $\gamma$ )	50 Kg	25 Kg	-	-
(II)-A dextrin having an average polymerization degree of 12.5 derived from amylopectin	-	-	-	90 Kg
(II)-B dextrin having an average polymerization degree of 25.0 derived from amylopectin	-	-	-	-
(III)-A dextrin having an average polymerization degree of 5.0	-	-	-	-
(III)-B dextrin having an average polymerization degree of 7.6	-	-	-	-
(III)-C dextrin having an average polymerization degree of 11.8	-	50 Kg	-	-
(III)-D dextrin having an average polymerization degree of 13.3	-	-	-	-
(III)-E dextrin having an average polymerization degree of 11.8	50 Kg	25 Kg	-	-
Average polymerization degree of a powdering carrier	9.2	10.5	6.0	11.9
Amount of acetic acid	20 Kg	20 Kg	20 Kg	20 Kg
Amount of water	80 Kg	80 Kg	80 Kg	80 Kg
Solubility of a powdering carrier	good	good	Note 1	good
Viscosity of solution cps (40°C)	85	115	-	110
Spray-drying aptitude	good	good	-	good
Amount of a produced powder (Kg)	116.7	116.3	-	117.0
Acetic acid content of a produced powder (%)	16.0	15.7	-	16.2
Acetic acid remaining ratio (yield) * (%)	93.4	91.3	-	94.8
Acetic acid stability (ratio) ** (%)	90	85	-	88
Caking resistance ***	Note 6	Note 6	-	Note 6

Table 5 (continued)

Powdering carrier	Test No.			
	9	10	11	12
(I)-A cyclic dextrin (100%α)	-	-	-	-
(I)-B cyclic dextrin (60%α, 25%β, 15%δ)	-	-	-	-
(II)-A dextrin having an average polymerization degree of 12.5 derived from amylopectin	100 Kg	50 Kg	-	-
(II)-B dextrin having an average polymerization degree of 25.0 derived from amylopectin	-	-	20 Kg	65 Kg
(III)-A dextrin having an average polymerization degree of 5.0	-	-	-	-
(III)-B dextrin having an average polymerization degree of 7.6	-	-	80 Kg	35 Kg
(III)-C dextrin having an average polymerization degree of 11.8	-	50 Kg	-	-
(III)-D dextrin having an average polymerization degree of 13.3	-	-	-	-
(III)-E dextrin having an average polymerization degree of 11.8	-	-	-	25 Kg
Average polymerization degree of a powdering carrier	12.5	12.2	11.1	18.9
Amount of acetic acid	20 Kg	20 Kg	20 Kg	20 Kg
Amount of water	80 Kg	80 Kg	80 Kg	80 Kg
Solubility of a powdering carrier	good	good	good	good
Viscosity of solution cps (40°C)	118	131	132	305
Spray-drying aptitude	good	good	good	Note 4
Amount of a produced powder (Kg)	116.7	116.4	116.4	117.0
Acetic acid content of a produced powder (%)	16.0	15.8	15.8	16.2
Acetic acid remaining ratio (yield) * (%)	93.4	92.0	92.0	94.8
Acetic acid stability (ratio) ** (%)	87	83	84	89
Caking resistance ***	Note 6	Note 6	Note 6	Note 6

## Example 1

The emulsion of a corn starch was hydrolyzed with  $\alpha$ -amylase by the following two-staged hydrolysis. When in the first stage the DE value reached 1.7 by the liquefaction with  $\alpha$ -amylase (Crystase KD supplied by Daiwa Kasel Kabushiki Kaisha), the hydrolysate was heated and boiled for inactivating  $\alpha$ -amylase and for swelling and dispersing starch, and in the second stage the resulting hydrolysate was added again with  $\alpha$ -amylase (Crystase KD) and further hydrolyzed to have a DE value of 7.2, and thereafter was dried to prepare the starch hydrolysate (moisture: 4 %) which had the saccharide composition comprising trace % G<sub>1</sub>, 1.4 % G<sub>2</sub>, 2.6 % G<sub>3</sub>, 2.4 % G<sub>4</sub>, 2.0 % G<sub>5</sub>, 2.3 % G<sub>6</sub>, 3.9 % G<sub>7</sub>, 3.7 % G<sub>8</sub> and 81.7 % G<sub>9 to n</sub> and had an average polymerization degree of about 14.

100 Kg of the obtained starch hydrolysate was dissolved in an aqueous acetic acid solution prepared by using 90 Kg of water and 30 Kg of acetic acid having a purity of 99 % and the resulting mixture was heated up to 55°C by a plate heater and sequentially spray-dried at a chamber temperature of 92°C to result in producing about 125 Kg of the powder having 20.6 % acetic acid content.

As the obtained powder has a high acetic acid content and moreover an excellent caking resistance, the obtained powder is very useful as an acidifying agent for providing an instant seasonings of various sauces or various soups.

## Example 2

In 250 Kg of water was dissolved 100 Kg of the starch hydrolysate (saccharide composition: 1.2 % G<sub>1</sub>, 5.3 % G<sub>2</sub>, 8.2 % G<sub>3</sub>, 5.4 % G<sub>4</sub>, 4.9 % G<sub>5</sub>, 9.3 % G<sub>6</sub>, 9.9 % G<sub>7</sub>, 5.1 % G<sub>8</sub> and 50.7 % G<sub>9 to n</sub>) having a DE value of 15, said starch hydrolysate being an article on the market. To the resulting solution, 10 g of magnesium sulfate, 70 g of primary potassium phosphate, 100 g of yeast extract, 50 g of peptone and 200 g of a baker's yeast were added and dissolved with stirring. The thus obtained solution was subjected to the cultivation which was carried out under the aeration of a sterile air at a rate of 60 ml/min. per liter of the solution at 30 ± 1°C for 48 hours. And the pH value of the solution was adjusted to 6.5 and thereafter the solution was heated up to 90°C for sterilization and moreover decolorized, desalted, deodorized and spray-dried to prepare 70 Kg of the starch hydrolysate (moisture: 3.5 %). This starch hydrolysate had the saccharide composition comprising trace % G<sub>1</sub>, 0.4 % G<sub>2</sub>, 5.4 % G<sub>3</sub>, 6.1 % G<sub>4</sub>, 5.3 % G<sub>5</sub>, 10.1 % G<sub>6</sub>, 10.8 % G<sub>7</sub>, 5.6 % G<sub>8</sub> 56.3 % G<sub>9 to n</sub> and had an average polymerization degree of about 8.9.

50 Kg of the obtained starch hydrolysate was mixed in 50 Kg of a wine vinegar (12.0 % acetic acid and 2.0 % extract) and the resulting solution was heated up to 50°C by a plate heater and sequentially spray-dried at a chamber temperature of 90°C to result in producing about 55 Kg of the powdery wine vinegar having an acetic acid content of 9.5 %. This powdery wine vinegar had flavour peculiar to a wine vinegar and had the good qualities in points of caking resistance, moisture proof, solubility etc..

## Example 3

In 200 Kg of an aqueous ethyl alcohol solution having an ethyl alcohol content of 60 w/w % was mixed 50 Kg of the starch hydrolysate (saccharide composition: 4.3 % G<sub>1</sub>, 5.5 % G<sub>2</sub>, 5.3 % G<sub>3</sub>, 5.6 % G<sub>4</sub>, 6.5 % G<sub>5</sub>, 5.5 % G<sub>6</sub>, 4.9 % G<sub>7</sub>, 4.3 % G<sub>8</sub> and 58.1 % G<sub>9 to n</sub>) having a DE value of 17.5, said starch hydrolysate being an article on the market. The resulting solution was allowed to stand for 24 hours to separate it into upper and lower two transparent layers. By fractionation, there were obtained 180 Kg of the upper layer and 70 Kg of the lower layer. This obtained lower phase (60 % solid and 15 % alcohol) was subjected to distillation by which alcohol was evaporated and recovered, and then subjected to drying to prepare about 40 Kg of the starch hydrolysate (moisture: 4.0 %). The starch hydrolysate had the saccharide composition comprising 1.4 % G<sub>1</sub>, 1.8 % G<sub>2</sub>, 3.4 % G<sub>3</sub>, 4.8 % G<sub>4</sub>, 5.5 % G<sub>5</sub>, 4.6 % G<sub>6</sub>, 5.1 % G<sub>7</sub>, 6.8 % G<sub>8</sub> and 66.6 % G<sub>9 to n</sub> and had an average polymerization degree of 13.1. 20 Kg of the obtained starch hydrolysate was mixed in 20 Kg of a rice vinegar (20 % acetic acid and 2.7 % extract) obtained by freeze-concentrating, and then the resulting mixture was heated up to 50°C by a plate heater and sequentially spray-dried at a chamber temperature of 92°C to result in producing about 24 Kg of the powdery rice vinegar having an acetic acid content of 14.7 %.

The obtained powder has aroma peculiar to a rice vinegar and moreover is of good quality in points of caking resistance, solubility, viscosity of its solution etc.. Therefore the obtained powder is compounded with sugar etc. to provide a very convenient powdery instant "san-baizu" which is a seasoning comprising vinegar, sugar and salt or soy sauce, or a very convenient "sushinomoto" which is a seasoning for "sushi".

## Example 4

The powdering carrier (average polymerization degree: 9.8, saccharide composition: 0.4 % G<sub>1</sub>, 1.1 % G<sub>2</sub>, 2.1 % G<sub>3</sub>, 2.3 % G<sub>4</sub> and 2.7 % G<sub>5</sub>), which comprising 30 Kg of the starch

hydrolysate (an article on the market) having an average polymerization degree of 11 and 80 Kg of the starch hydrolysate containing 50 % the acyclic starch hydrolysate having an average polymerization degree of 12 and 50 % the cyclic oligosaccharide (mixture of 60 %  $\alpha$ , 25 %  $\beta$  and 15 %  $\gamma$ ) obtained by hydrolyzing a potato starch with  $\alpha$ -amylase and thereafter making a cyclic oligosaccharide-forming enzyme act on, was mixed in the solution comprising 20 Kg acetic acid having a purity of 99 % and 100 Kg of "shuseizu" (15.0 % acetic acid, 0.5 % extract and 84.5 % water), and thereby the solution (viscosity: 105 cps at 40°C) was obtained.

And then the resulting solution was heated up to 60°C by a plate heater and sequentially spray-dried at a chamber temperature of 95°C by a spray drier having a nozzle style to result in producing about 140 Kg of the powdery product.

The obtained powder was the powdery acetic acid having a high, viz., 23.0 % acetic acid content. The obtained powder is mixed with salt, sugar, a powdery seasoning etc. to provide an instant "sushizu" which is a vinegar for sushi, "nihaizu" which is a seasoning comprising salt or soy sauce and vinegar, or "sanbaizu". By subjecting the hermetically sealed pouches, in which these mixed products being severally enclosed, to a storage test, it was found that each acetic acid stability, viz., antivolatility, caking resistance etc. were superior to those of the products obtained by the conventional method.

#### Example 5

In 100 Kg of wine vinegar (12.0 % acetic acid, 2.0 % extract and 86.0 % water) was mixed the powdering carrier (average polymerization degree: 14.6 %, and saccharide composition: trace %  $G_1$ , 1.6 %  $G_2$ , 3.0 %  $G_3$ , 3.2 %  $G_4$  and 3.2 %  $G_5$ ) comprising 80 Kg of the starch hydrolysate (an article on the market) having an average polymerization degree of 10 and 20 Kg of the starch hydrolysate having an average polymerization degree of 33 which was obtained by hydrolyzing a waxy starch with  $\alpha$ -amylase, and thereby the solution (viscosity: 120 cps at 40°C) was obtained.

And then this solution was heated up and sequentially dried at a chamber temperature of 100°C by a spray drier to produce about 110 Kg of the powdery product. This obtained powdery product had an acetic acid content of 10.2 % and was the powder having flavor peculiar to a wine vinegar. This powder can be used as a powdery table vinegar or as a material for various European style seasonings such as a powdery mixed dressing, a powdery mixed sauce etc.. The mixture prepared by mixing the obtained powder with sugar, salt, amino acid etc. was good in an acetic acid stability and showed no caking.

#### Example 6

In 60 Kg of a cider vinegar (20.0 % acetic acid, 2.5 % extract and 77.5 % water) obtained by freeze-concentrating was dissolved the powdering carrier (average polymerization degree: 12.2, saccharide composition: 0.3 %  $G_1$ , 0.8 %  $G_2$ , 1.8 %  $G_3$ , 2.1 %  $G_4$  and 2.4 %  $G_5$ ) comprising 20 Kg of the starch hydrolysate having an average polymerization degree of 18 which was obtained by hydrolyzing a waxy starch with  $\alpha$ -amylase and 40 Kg of the starch hydrolysate containing 50 % the acyclic starch hydrolysate having an average polymerization degree of 12 and 50 % the cyclic oligosaccharides (average polymerization degree: 6.5) obtained by liquefying a potato starch with  $\alpha$ -amylase and thereafter making a cyclic oligosaccharide-forming enzyme act on. The resulting solution (viscosity: 75 cps at 60°C) was heated up to 60°C by a plate heater and sequentially spray-dried at a chamber temperature of 95°C to result in producing about 71 Kg of the powdery product. This obtained powdery product had an acetic acid content of 15.8 % and the loss of acetic acid caused by drying was very little, viz., the acetic acid remaining ratio was 94 %. This obtained powder is the powdery brew vinegar having aroma peculiar to a cider vinegar and can be used as a material for various instant seasoning or confectionary.

#### Example 7

In the solution comprising 50 Kg of a cider vinegar (12.0 % acetic acid and 1.5 % extract), 50 Kg of "shuseizu" (15.0 % acetic acid and 0.5 % extract), 60 Kg of a soy sauce (14.5 % extract and 16.0 % salt) and 20 Kg of a liquid extract (10 % extract) of dried bonito was dissolved 140 Kg of the starch hydrolysate (0 %  $G_1$ , 2.6 %  $G_2$ , 2.6 %  $G_3$ , 2.4 %  $G_4$  and 2.2 %  $G_5$ ) having an average polymerization degree of 12.5 which was prepared by hydrolyzing a waxy starch with  $\alpha$ -amylase. The resulting solution was heated up to 65°C and sequentially spray-dried at a chamber temperature of 100°C to result in producing about 170 Kg of the powdery product.

This obtained powder has 7.0 % acetic acid content, 5.6 % salt content and 6.8 % various extracts, and is dissolved in water to provide "ponzu" having flavor peculiar to dried bonito, which "ponzu" is originally a vinegar added with juice of a citrus fruit.

This powdery product contains salt and various extracts besides acetic acid, and is good in keeping acetic acid and other flavors and moreover very good in caking resistance.

## CLAIMS

1. A process for powdering a liquid seasoning containing acetic acid which comprises mixing a starch hydrolysate containing not more than 20 % oligosaccharides having a glucose polymerization degree of not more than 5 and not more than 7 % oligosaccharides having a glucose polymerization degree of not more than 3 in the liquid seasoning containing acetic acid in an amount of not less than 70 % of the amount of the water contained in the liquid seasoning containing acetic acid and spray-drying the resulting solution. 5
2. A process according to claim 1 wherein the starch hydrolysate having an average polymerization degree of 6 to 18 and also inducing viscosity of not more than 300 cps at 40°C in the case of a 50 % aqueous solution of the starch hydrolysate is used. 10
3. A process according to claim 1 wherein the starch hydrolysate contains not more than 15 % oligosaccharides having a glucose polymerization degree of not more than 5 and not more than 5 % oligosaccharides having a glucose polymerization degree of not more than 3. 15
4. A process according to claim 1 wherein the starch hydrolysate contains at least one member selected from the group consisting of the following a, b, c and d: 15
  - a. a starch hydrolysate prepared by hydrolyzing starch composed of amylopectin and amylose,
  - b. a starch hydrolysate prepared by hydrolyzing starch composed of amylopectin,
  - c. a starch hydrolysate containing cyclic oligosaccharides and acyclic starch hydrolysate, said
  - 20 a starch hydrolysate being prepared from starch composed of amylopectin and amylose, and 20
  - d. a starch hydrolysate containing cyclic oligosaccharides and acyclic starch hydrolysate, said a starch hydrolysate being prepared from starch composed of amylopectin.
5. A process according to claim 1 wherein the starch hydrolysate contains at least one member selected from the group consisting of  $\alpha$ -cyclic oligosaccharide,  $\beta$ -cyclic oligosaccharide and  $\gamma$ -cyclic oligosaccharide, said at least one member being added. 25
6. A process according to claim 1 wherein the liquid seasoning containing acetic acid is selected from the group consisting of rice vinegar, "kasuzu", "shuseizu", malt vinegar, wine vinegar, cider vinegar, synthesized vinegar, aqueous solution of the abovementioned matters, each abovementioned matter added with acetic acid and each processed solution of the 30
- abovementioned matters. 30